

ABSTRACT

An experimental study on the effect of carbon dioxide (CO_2) dilution on flammability limit of acetylene (C_2H_2) was performed, for system with various concentration of fuel. The objectives of this experiment were to determine the lower flammability limit (LFL) and upper flammability limit (UFL) of C_2H_2 and to determine the effect of CO_2 on flammability limits of C_2H_2 . The explosion pressure and explosion time were measured using an apparatus called 20 L explosion vessel at operating condition 20°C and 1 bar. The first part of this experiment was conducted with different percentages of C_2H_2 without the presence of CO_2 to determine the LFL and UFL of pure acetylene at temperature 20°C and pressure 1 bar. The second part was conducted with different percentage of C_2H_2 with the presence of 15% of CO_2 . From the theory, when there is dilution of inert gases in fuel happen, the LFL of the fuel will increase while the UFL of the fuel will decreases, thus the flammability range of those fuel will be smaller. The explosion pressure data was collected to determine the flammability limit of acetylene and also acetylene with the presence of CO_2 .

ABSTRAK

Satu kajian eksperimen tentang kesan pencairan karbon dioksida (CO_2) pada had kemudahbakaran asetilena (C_2H_2) dilakukan, untuk satu sistem dengan pelbagai kepekatan bahan api. Objektif eksperimen ini adalah untuk menentukan kemudahbakaran had yang lebih rendah (LFL) dan had kemudahbakaran atas (UFL) C_2H_2 dan untuk menentukan kesan CO_2 terhadap kemudahbakaran C_2H_2 . Tekanan letupan dan masa letupan diukur menggunakan radas yang dipanggil 20 L bekas letupan pada keadaan operasi $20\text{ }^\circ\text{C}$ dan 1 bar. Bahagian pertama daripada eksperimen dijalankan dengan peratusan C_2H_2 yang berbeza tanpa kehadiran CO_2 untuk menentukan LFL dan UFL asetilena tulen pada suhu $20\text{ }^\circ\text{C}$ dan tekanan 1 bar. Bahagian kedua dijalankan dengan peratusan C_2H_2 yang berbeza dengan kehadiran 15 % CO_2 . Berdasarkan teori, apabila terdapat pencairan gas lengai dalam bahan api berlaku, LFL bahan api akan meningkat manakala UFL bahan api akan berkurangan, dengan itu had terbakar bahan api akan menjadi lebih kecil. Tekanan letupan data dikumpul untuk menentukan had kemudahbakaran asetilena dan juga asetilena dengan kehadiran CO_2 .

TABLE OF CONTENTS

	Page
SUPERVISOR'S DECLARATION	i
STUDENT'S DECLARATION	ii
ACKNOWLEDGEMENTS	iv
ABSTRACT	v
ABSTRAK	vi
TABLE OF CONTENTS	vii
LIST OF TABLES	x
LIST OF FIGURES	xi
LIST OF SYMBOLS	xii
LIST OF ABBREVIATIONS	xiii

CHAPTER 1 INTRODUCTION

1.1	Background of Study	1
1.2	Problem Statement	2
1.3	Objectives	2
1.4	Scope of Study	3
1.5	Significance of Study	3

CHAPTER 2 LITERATURE REVIEW

2.1	Acetylene (C ₂ H ₂)	4
2.2	Carbon Dioxide (CO ₂)	6
2.3	Flammability Limits	8
2.4	Inerting Process	11
2.5	Diluents Effect	12
2.6	Limiting Oxygen Concentration (LOC)	12
2.7	Previous Work/Research	13

2.7.1	The Limiting Oxygen Concentration and Flammability Limits of Gases and Gas Mixtures	13
2.7.2	Extended Le Chatelier's Formula for Carbon Dioxide Dilution Effect on Flammability Limits	15
2.7.3	Effects of Carbon Dioxide on Explosion Limits of Flammable Gases in Goafs	17
2.7.4	Additive Effects on Explosion Pressure and Flame Temperature of Stoichiometric Ethylene-air Mixture in Cloud Vessels	18

CHAPTER 3 METHODOLOGY

3.1	Introduction	19
3.2	Experimental apparatus	19
3.2.1	A 20-L-Fire Explosion Vessel	19
3.2.2	Measurement and Control System KSEP 332	20
3.3	Raw Materials and Setting Condition	21
3.4	Experimental Procedure	22

CHAPTER 4 RESULT AND DISCUSSION

4.1	Explosion of Acetylene (C_2H_2) without presence of Diluents	25
4.2	Explosion of Acetylene (C_2H_2) with Presence of 15 vol. % Carbon Dioxide (CO_2)	28
4.3	Comparison of the Data	29
4.4	Comparison with Previous Work	32

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS

5.1	Conclusion	34
5.2	Recommendations	34

REFERENCES	35
APPENDICES	
A	
Data from software for pure Acetylene + air at operating pressure 1 bar	38
B	
Data from software for Acetylene + 15 % carbon dioxide + air at operating pressure 1 bar	53

LIST OF TABLES

Table No.	Title	Page
2.1	Properties of Acetylene	4
2.2	Flammability limits for some common gases	5
2.3	Properties of carbon dioxide	7
2.4	Flammability/LOC: 120-L and 20-L closed vessel results vs. 12-L glass sphere and flammability tube	14
2.5	LOC: fuel mixtures containing methane: CH ₄ -H ₂ ; CH ₄ -CO; CH ₄ -C ₂ H ₄ ; CH ₄ -1:1 CO:H ₂ ; experimental vs. calculated	15
2.6	Observed values of flammability limits for fuel-carbon dioxide mixtures of eight kinds of fuels	16
3.1	Setting condition	21
3.2	Guidance for symbols	22
4.1	Summary of P _m and dP/dt of acetylene explosion	25
4.2	Summary of P _m and dP/dt of acetylene explosion	28
4.3	Comparison data of LFL, UFL, P _{max} and dP/dt between explosion of acetylene with and without the presence of carbon dioxide	30
4.4	Comparison between present studies with previous study	32

LIST OF FIGURES

Figure No.	Title	Page
2.1	Fire triangle	8
2.2	Flammable Range	9
2.3	Example of LEL and UEL of gasoline	10
3.1	Schematic Diagram of 20-L-Fire Explosion Vessel	20
3.2	The KSEP 332	21
3.3	20-L-Fire Explosion Vessel	22
3.4	Diagram of Igniter between the Electrode Rods	23
3.5	KSEPT 6.0	23
3.6	Experimental Work Flows	24
4.1	Graph of corrected pressure, P_m (bar) versus vol. % acetylene	27
4.2	Graph of corrected pressure, P_m (bar) versus vol. % acetylene	29
4.3	Comparison between explosion of acetylene with and without presence of CO_2	31

LIST OF SYMBOLS

°C	Celcius
J	Joule
K	Kelvin
O ₂	Oxygen
Vol. %	Percentage by volume

LIST OF ABBREVIATIONS

C_2H_2	Acetylene
CO_2	Carbon Dioxide
LFL	Lower Flammability Limit
UFL	Upper Flammability Limit
LOC	Limiting Oxygen Concentration
IE	Ignition energy
P_{exp}	Explosion overpressure: the difference between the pressure at ignition time (normal pressure) and the pressure at the culmination point is the maximum explosion overpressure P_{ex} measured in the 20-L-apparatus at nominal fuel concentration.
P_{max}	Maximum explosion overpressure: Maximum value of P_m determined by test over a wide range of fuel concentrations
t_l	Duration of combustion: time differences between the activation of the ignition and the culmination point
t_v	Ignition time delay: t_v influences the degree of turbulence. This is the most important control parameter
P_m	Corrected explosion overpressure: Due to cooling and pressure effects caused by the chemical igniters in the 20-L-apparatus, the measured explosion overpressure P_{ex} has to be corrected

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Knowing the flammability limits of flammable substances are crucial knowledge as it is related to safety of the substances. Flammability limits is one of important features in development of safe practices for handling a flammable vapor or gas. It is a crucial issue in research on processing and storing organic matter safely (Chen et al., 2008). Flammability limits studies also are important for assessment of fire safety in many environments and determining the operation limits of combustion devices (Ju, Masuya and Rooney, 1998).

Different methods have been proposed to predict the flammability limits, especially the lower flammability limit for pure flammable gases. Complex gaseous mixtures, for which the Le Chatelier equation is regularly used to estimate the flammability limits, are also consumed or formed in normal and emergency situation in process industries (Chen et al., 2008). Thus, to know the effect of carbon dioxide (CO_2) on the explosion characteristics of acetylene (C_2H_2) is a need for a better handling, storage and processing of the substances.

There are way to predict the upper and lower flammability limits of mixture composed of hydrocarbon and inert CO_2 (Chen et al., 2008). The experiment that has been carried out studies on the CO_2 effects on lower flammability limit (LFL) and upper flammability limit (UFL) of C_2H_2 . There are linear relations between reciprocal of upper or lower flammability limits and reciprocal of molar fraction of hydrocarbons in hydrocarbons/inert gas mixture (Chen et al., 2008).

C_2H_2 which has been used as fuel in this experiment is a colorless and odorless substance which has the flammability range of 2.50 vol. % to 81 vol. % (Coward and Jones, 1952). C_2H_2 when liquefied, compressed, heated or mixed with air will become highly explosive especially in the presence of open flames, sparks or heat (Stacey, 2002; Foxall, 2009).

1.2 Problem statement

Today industries are now more concern about the safety handling of chemical substances. Flammable substances were given more attention in order to keep a healthy and safe working place. There are incidents of fire disasters in chemical and petrochemical plants caused by the leak of materials at or above their auto ignition temperature or flash point or within their flammability limit (Tareq, 2003). The operation of tank filling and emptying or more generally speaking, of process or transportation equipment, involving flammable substances, have traditionally been quoted as very dangerous, as they involve very serious fire and explosion risks (Planas-Cuchi et al., 1999).

C_2H_2 is an extremely flammable substance in the presence of open flames, sparks and heat. It is widely used in industry as a raw material in production of other chemical (Foxall, 2009). The flammability limits characteristic of chemical substances is a crucial knowledge for safety handling, storage and also processing activities.

Due to this problem, dilution with nitrogen and carbon dioxide is a typical way of ensuring safety in the use of flammable gases (Kondo et al., 2006). Therefore, to know the effects of inert gas, in this case CO_2 , on flammability limits of C_2H_2 is a need.

1.3 Objectives

There are two objectives in this study to be achieved. The two objectives are as follows:

- (a) To determine the LFL and UFL of acetylene
- (b) To determine the effect of CO_2 on flammability limits of C_2H_2

1.4 Scope of Study

The scopes of the study of this project are as follows:

- 1) The fixed variables were pressure and temperature which fixed at 1 bar absolute and 20 °C respectively. The pressure and temperature was maintained to avoid disturbance in the results obtained.
- 2) The manipulated variable in this experiment was volume percentage of CO₂ (0 vol. % and 15 vol. %) use in explosion. The percentage of CO₂ was varied to study the effects of CO₂ on the flammability limits of C₂H₂.
- 3) The controlled variables are LFL and UFL of C₂H₂. The LFL and UFL were observed and discuss to evaluate the effects of manipulated variables.

1.4 Significance of the Study

This study is related mostly about the safety handling, storage and processing of C₂H₂. As C₂H₂ is widely used in process industries, in oxy-acetylene welding and metal cutting, safety matter of the C₂H₂ must be taken into consideration. Hristova and Tchaoushev (2006) stated that flash point and flammability limits are important factors in the development of safe practices for handling and storage of pure substances and mixtures. Regulatory authorities use data for flash point in order to classify flammable and combustible substances (Hristova and Tchaoushev, 2006).

Mixtures at different temperatures and pressures are used in industrial activities. The flash point can be used to determine the level of risk in different stages of the process. Knowledge of flammability limits at elevated temperatures and pressures is needed in order to ensure safe and economically acceptable operation of chemical processes (Hristova and Tchaoushev, 2006).

By finding the effect of CO₂ on C₂H₂ and percentage of CO₂ that can reduce the possibility of explosion of acetylene, the safety precautions can be taken into consideration.

CHAPTER 2

LITERATURE REVIEW

2.1 Acetylene (C_2H_2)

Acetylene (C_2H_2) is a colorless, odorless and flammable gas. The other names of C_2H_2 are ethine and ethyne (Foxall, 2009). Table 2.1 shows some of the properties of C_2H_2 .

Table 2.1: Properties of acetylene

Property	Value
Molecular weight (g/mol)	26.04
Specific gravity	920
Flammable limits (vol. %)	2.5 – 81
Density (kg/m^3)	1.097

Source: Engineering Toolbox Data (2011)

C_2H_2 is use in industry as a raw material in other chemicals production such as acetaldehyde and vinyl chloride. Most common use of C_2H_2 is as raw material for the production of various organic chemical, including 1,4-butanediol, which is widely used in the preparation of polyurethane and polyester plastics (Stacey, 2002). C_2H_2 also used as a fuel in oxy-acetylene welding and metal cutting (Foxall, 2009; Stacey, 2002).

C_2H_2 has the highest flame temperature of any common hydrocarbon because of its triple-bond structure $H-C\equiv C-H$. Combustion with oxygen achieves a flame temperature of 5580 °F (3087 °C), releasing 1470 BTUs per cubic foot. Its high flame

temperature allows it to be used in a variety of metal working applications like cutting, welding, brazing, and soldering (Airgas Data, 2012).

Acetylene's chemical and physical properties account for many of its uses. Its flame is highly luminous, thus it was used in miners, bicycle, automobile and streets lamps (O'Hara, 1997).

Combustion of C_2H_2 in pure oxygen produces the highest achievable flame temperature, over 3300 °C, releasing 11,800 J/g, allowing it to weld, cut, braze and solder metals in various environments. The oxy-acetylene torch is used to repair ships underwater, to construct bridges, pipelines, dams, tunnels, buildings and to reinforce concrete (O'Hara, 1997).

Exposure to C_2H_2 is most likely to occur in an occupational setting where it is produced and used. Exposure of C_2H_2 in the home is very unlikely as it is not used domestically (Foxall, 2009).

Storing and handling of C_2H_2 must with great care. When it is transported through pipelines, the pressure is kept very low and the length of the pipeline is very short. When acetylene must be pressurized and stored for use in oxy-acetylene welding and metal cutting operations, special storage cylinders are used. The cylinders are filled with an absorbent material, like diatomaceous earth, and a small amount of acetone (Stacey, 2002). Table 2.2 listed the flammability limits of some common gases used as fuel in combustion process.

Table 2.2: Flammability limits for some common gases

Gas or Vapor	Limits in air, %		Limits in Oxygen, %	
	Lower	Higher	Lower	Higher
Methane	5.3	15.0	5.1	61
Ethane	3.0	15.0	3.0	66
Propane	2.2	9.5	2.3	55
Butane	1.9	8.5	1.8	49

Table 2.2: Continued

Gas or Vapor	Limits in air, %		Limits in Oxygen, %	
	Lower	Higher	Lower	Higher
Isobutane	1.8	8.4	1.8	48
Pentane	1.5	7.8	-	-
Isopentane	1.4	7.6	-	-
Acetylene	2.5	81	-	-
Hydrogen	4.0	75	4.0	9.4
Toluene	1.4	6.7	-	-
Gasoline	1.4	7.6	-	-
Kerosene	0.7	5	-	-

Source: Coward and Jones (1952)

In this experiment, C_2H_2 was used concerning that acetylene has wide range of flammability limits which make it highly flammable especially with the presence of sparks, heat or open flames (Foxall, 2009). There are hazardous situations that can occur during filling or emptying operations which associates with the release and evaporation of flammable gases due to the rupture of a flexible hose or pipe through which the filling or emptying is being performed. The hazards of this situation are pool-fire, or if there is a delay in ignition, the formation of a flammable cloud will occur. Fire and explosion, together with release, are the most common accidents in filling or emptying operations (Planas-Cuchi, 1999). Thus, this make the selection of acetylene in this study is reasonable as it is highly flammable may caused undesired explosion if not properly handled and stored.

2.2 Carbon Dioxide (CO_2)

Carbon dioxide (CO_2) is a molecule with the molecular formula CO_2 (Black, 1750). CO_2 is an odourless and colourless gas (Sickler, 1995). Although CO_2 mainly consists in the gaseous form, it also has a solid and a liquid form. It can only be solid when temperatures are below $-78\text{ }^{\circ}C$. Liquid CO_2 mainly exists when CO_2 is dissolved in water. CO_2 is only water-soluble, when pressure is maintained. After pressure drops, the CO_2 gas will try to escape to air. This event is characterized by

the CO₂ bubbles forming into water (Black, 1750). Table 2.3 shows the properties of CO₂.

Table 2.3: Properties of Carbon Dioxide

Property	Value
Molecular weight	44.01
Specific gravity	1.53 at 21 °C
Critical density	468 kg/m ³
Concentration in air	370,3 * 10 ⁷ ppm
Stability	High
Liquid	Pressure < 415.8 kPa
Solid	Temperature < -78 °C
Henry constant for solubility	298.15 mol/ kg * bar
Water solubility	0.9 vol/vol at 20 °C

Source: Black (1750)

CO₂ has important uses in the home and in industry. For example, CO₂ released by baking powder or yeast makes cake batter rise. CO₂ in soft drinks, beer, and sparkling wines gives the beverages their fizz. Some fire extinguishers use CO₂ because it does not burn and because pure carbon dioxide is denser than air. CO₂'s heaviness enables it to blanket a fire and prevent oxygen from getting to the fire (Sickler, 1995).

Dry ice is solid CO₂. CO₂ becomes a solid at -78.5 °C. The name dry ice refers to the fact that the substance changes from a solid to a gas without first becoming a liquid. Because of this property, dry ice is widely used in industry to refrigerate food, medicine, and other materials that would be damaged by the melting of ordinary ice (Sickler, 1995).

In this research, CO₂ is an inert gas that acts as diluents in the reaction of C₂H₂ with igniter. The CO₂ will be used in inerting process, where it will reduce percentage of oxygen (Planas-Cuchi et al., 1999; Crowl and Louvar, 2002). Alteration of upper flammability limit due to CO₂ dilution is larger than the ones for nitrogen dilution (Kondo, 2006). The addition of CO₂ in flammable gas (for this case is C₂H₂) will alter the flammability limit of C₂H₂.

2.3 Flammability limits

Flammability limits can be defined as concentration range in which a flammable substance can produce a fire or explosion when an ignition sources (such as a spark or open flame) is present (Toreki, Restivo and Gil, 2010). Flammability limits also can be defined as a range of fuel and air proportion in which combustion can be self-sustaining (Md Noor, 2011). Zlochower and Green (2006) defined flammability limits as the limiting fuel concentrations in air that can support flame propagation and lead to an explosion. Fuel concentrations outside those limits are non-flammable. In other word, flammability limit can be defined as the range of those flammable substances can produce fire or explosion if an ignition sources is present.

For an explosion to occur, there are three things needed called fire triangle. There are source of fuel (e.g., flammable gas or vapor), air (oxygen) and a source of ignition (e.g., spark, open flame, or high-temperature surface). Figure 2.1 shows the three components needed for an explosion to occur.

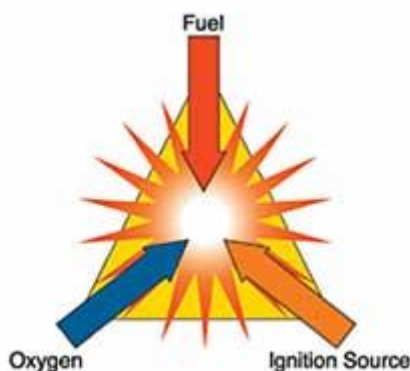


Figure 2.1: Fire triangle

Source: Holcom (2005)

The three components shown in Figure 2.1 which are fuel, oxygen and ignition source must present for an explosion to occur. Correct amount of fuel and oxygen,

molecularly mixed fuel and oxygen, and minimum ignition energy are the requirements for successful combustion or explosion (Md Noor, 2011).

Flammability limits has two types which are lower flammability limit (LFL) and upper flammability limit (UFL). Lower explosive limit (LEL) and upper explosive limit (UEL) are used interchangeably with LFL and UFL (Crowl and Louvar, 2002). When the combustion of the fuel is not controlled within the confines of the burner system, the limits of flammability can be called the explosive limits (Md Noor, 2011). Figure 2.2 shows the flammable range of flammable substances.

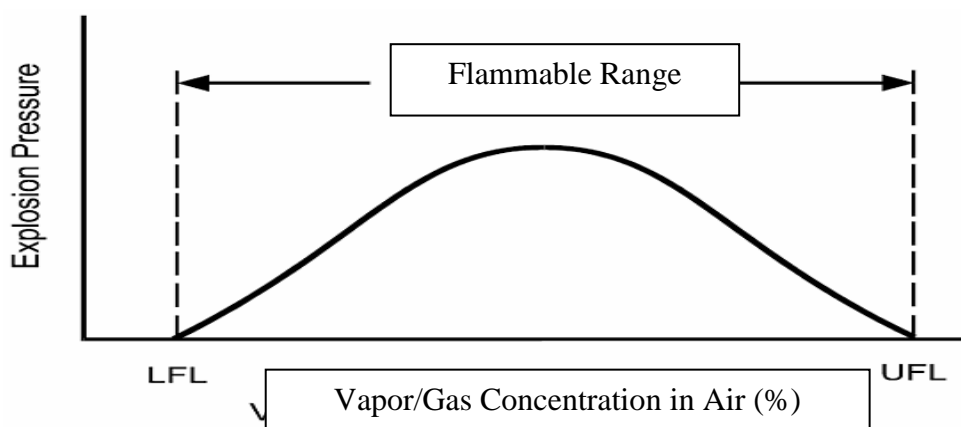


Figure 2.2: Flammable range

Source: Michaels et al. (2012)

LFL means the mixture with the smallest fraction of combustible gas and still can explode. The UFL means the mixture with the richest fraction of combustible gas and can still explode. When the mixture is below LFL, that mixture is too lean to burn. In this state, there is not enough fuel to continue an explosion and explosion cannot occur even if a source of ignition is present. Above the UFL, that mixture is too rich to burn (Chen et al., 2008). Figure 2.3 shows LEL versus UEL.

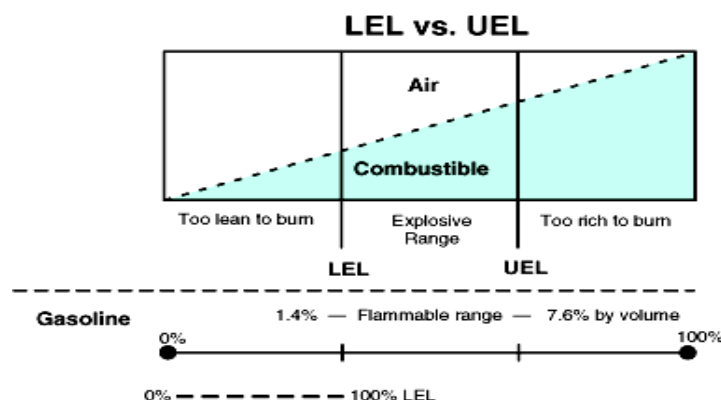


Figure 2.3: Example of LEL and UEL of Gasoline

Source: Wallace (2009)

Figure 2.3 illustrated the explosive range for gasoline. Below LEL, the mixture is too lean to burn and above the UEL, the mixture is too rich to burn. The explosion only occurs in between LEL and UEL (Wallace, 2009).

Flammability limits are one of the important features in the development of safe practices for handling a flammable vapor or gas. For this reason, they constitute a crucial research on processing and storing organic matter safely. Different methods have been proposed to predict the flammability limits, especially the LFL, for pure flammable gases. However, it is known that values of flammability limits are dependent upon the experimental apparatus and condition used for the measurement (Chen et al., 2008).

Le Chatelier's formula is commonly used to predict the flammability limits of blended gases of various fuels. Le Chatelier's formula can very well predict the values of lower flammability limits and can reasonably well predict the upper flammability limits (Kondo, 2006). Le Chatelier's formula is expressed in Eq. (2.1)

$$\frac{1}{l} = \frac{c1}{l1} + \frac{c2}{l2} + \frac{c3}{l3} + \dots + \frac{cn}{ln} \quad (2.1)$$

L : Flammability limits of mixtures by volume % (LFL & UFL)

- C : Concentration of component, i in the gas mixture
l : Flammability limits of component, i by volume % (LFL & UFL)

The traditional criterion used in the US, which was the basis of an extensive database of flammability limits, required that flame and explosion propagation be distinguished from ignition phenomena (Coward and Jones, 1952; Kuchta, 1985). The flammability limit is a widely used index for representing flammability of gases and vapors. LFL is important for risk evaluation in the chemical industry (Cesana and Siwek, 2011).

2.4 Inerting Process

Inerting process is the process of adding an inert gas to a combustible mixture to reduce the concentration of oxygen below the limiting oxygen concentration (LOC) for the purpose of lowering the likelihood of explosion. The inert gases that usually have been used are nitrogen, carbon dioxide and sometimes steam. This inert gas does not take part in the reaction mechanism (Chen et al., 2008).

Inerting process is to alter the flammability limit and in turn to reduce the possibility of explosion or catching fire (Crawl and Louvar, 2002; Planas-Cuchi et al., 1999). The progressive addition of an inert gas to a fuel-air mixture causes the narrowing of the flammability range to the point where two limits coincide (Zlochower and Green, 2009). Inerting process commonly used to bring the oxygen concentration below 4 % (Crawl and Louvar, 2002).

Procedure of diluting a combustible gas with inert gas could be also taken as a mixing process of fuel and inert gas. Inert gas does not take part in the combustion kinetics; it seems possible that we could explain the inert gas dilution effects on the flammability limits from the viewpoint of physical principles only. In this study, the carbon dioxide dilution effects on the flammability limits for pure hydrocarbons are explored (Chen et al., 2008).

If the percentage of oxygen in the reaction of flammable gas is low, the possibility of explosion will be reduced. This is due to concentration of oxygen which is below stoichiometric.

2.5 Diluents effect

Diluents have been significantly used in industries today. The presence of diluents in methane, which is often encountered in practice, brings about significant changes in the combustion process in engines and undermines performance. The presence of diluents with methane reduces the effective heating value of the fuel mixture when the energy releases by the oxidation reactions of the fuel component is shared with diluents (Shrestha and Karim, 2000).

Dilution with nitrogen is a typical way of ensuring safety in the use of flammable gases. CO₂ is another typical gas to be used for the same purposes (Kondo et al., 2006). The alterations of UFL due to CO₂ dilution are larger than the ones for nitrogen dilution as well (Kondo et al., 2006). CO₂ is more effective than nitrogen as diluents due to its higher molar heat capacity.

2.6 Limiting Oxygen Concentration (LOC)

The maximum oxygen amount of a non-flammable fuel–air–inert mixture is the LOC (limiting oxygen concentration), an important safety characteristics. LOC which stands for limiting oxygen concentration is same as the minimum oxygen concentration. It is the limiting concentration of CO₂ below which combustion is not possible, independent of the concentration of fuel. The unit for limiting oxygen concentration is volume percent of oxygen. It varies with temperature and pressure and dependent on type of inert (non-flammable) gas (Razus et al., 2005).

Zlochowar and Green (2009) stated that the limiting oxygen concentration (LOC) is the minimum oxygen concentration in a mixture of fuel, air, and an inert gas that will propagate flame. In practice, the limits (LFL, UFL, and LOC) represent an

average between the neighboring concentrations inside and outside the experimental flammability limits.

When concentration of inert gas increased, the oxygen concentration decreases. When oxygen concentration below limiting oxygen concentration (LOC), flammable gas can be safely admitted to the vessel because the possibility of internal explosion has been eliminated.

2.7 Previous Work/Research

2.7.1 The Limiting Oxygen Concentration and Flammability Limits of Gases and Gas Mixtures

Zlochower and Green (2009) study on the limiting (minimum) oxygen concentration (LOC), in the presence of added nitrogen of methane (CH_4), propane (C_3H_8), ethylene (C_2H_4), carbon monoxide (CO), and hydrogen (H_2). This study also addresses the issue of the flammable concentration (flammability) limits of these pure gases in air. The study was conducted based on spark ignited explosion in large, spherical laboratory vessels (120-L and 20-L). The results obtained are compared with the older values which used long flammability tubes with a diameter more or equal to 5 cm. the results also compared with the results from 12-L spherical flask with a visual flame propagation criterion.

From the obtained results and comparison, 120-L and 12-L results show excellent agreement with 20-L results and also with earlier flammability tube values for lower flammability limits.

Table 2.4 and 2.5 summaries the comparison between 120-L, 20-L, 12-L, and flammability tubes results.

Table 2.4: Flammability/LOC: 120-L and 20-L closed vessel results vs. 12-L glass sphere and flammability tube

Fuel (F)	Vessel	Stoichiometric eq.	Mole ratio (O ₂ /F)	LFL (mol %)	UFL (mol %)	LOC (N ₂) (mol %)
Hydrogen (H ₂)	120-L	$2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$	0.5	7	75.9	4.6
	20-L Flam. tube			6 4	75.0	4.7 5.0
Carbon monoxide (CO)	120-L	$2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$	0.5	12.2	72.0	5.1
	12-L Flam. tube			12.2 12.5	72.5 74.0	5.5
Methane (CH ₄)	120-L	$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	2	5.0	15.8	11.1
	20-L			4.9	15.9	10.7
	12-L			4.9	15.8	11.3
	Flam. tube			5.0	15.0	12.0
Ethylene (C ₂ H ₄)	120-L	$\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$	3	2.7	31.4	8.5
	12-L			2.7	31.5	8.6
	Flam. tube			2.7	36.0	10.0
Propane (C ₃ H ₈)	120-L	$\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$	5	2.0	9.8	10.7
	12-L			2.0	10.0	10.5
	Flam. tube			2.1	9.5	11.5

Source: Zlochower and Green (2009)

Table 2.5: LOC: fuel mixtures containing methane: CH₄ – H₂; CH₄ – CO; CH₄ – C₂H₄; CH₄-1:1 CO:H₂; experimental vs. calculated

Fuel: %	CH ₄ -H ₂		CH ₄ -CO		CH ₄ -Ethylene		CH ₄ -1:1 CO:H ₂	
	(LOC) _{exp}	(LOC) _{calc}	(LOC) _{exp}	(LOC) _{calc}	(LOC) _{exp}	(LOC) _{calc}	(LOC) _{exp}	(LOC) _{calc}
CH₄								
0	4.6	4.6	5.1	5.1	8.6	8.6	4.8	4.8
10	6.5	5.6	6.1	6.1	8.6	8.7	-	-
20	-	-	-	-	-	-	7.3	6.7
25	7.7	6.9	7.8	7.4	8.9	9.0	-	-
35	8.3	7.65	-	-	-	-	-	-
40	-	-	-	-	-	-	8.7	8.2
50	9.1	8.64	9.5	9.0	9.3	9.45	-	-
60	-	-	-	-	-	-	9.7	9.4
75	10.3	10	10.9	10.2	10.05	10.1	-	-
80	-	-	-	-	-	-	10.5	10.3
90	10.9	10.7	11	10.8	-	-	-	-
100	11.1	11.1	11.1	11.1	11.1	11.1	11.1	11.1

Source: Zlochower and Green (2009)

2.7.2 Extended Le Chatelier's Formula for Carbon Dioxide Dilution Effect on Flammability Limits

Kondo et al. (2006) conducted a study to measure CO₂ dilution effect on the flammability limit for various flammable gases. The Le Chatelier's formula as shown in eq. (2.2) is commonly used to predict the flammability limits of blended gases of various fuels.

$$\frac{1}{L} = \frac{c_1}{l_1} + \frac{c_2}{l_2} + \frac{c_3}{l_3} + \dots + \frac{c_n}{l_n} \quad (2.2)$$

The famous Le Chatelier's formula is modified to be used for calculation of flammability limits with the presence of diluents. Dilution with CO₂ is a typical way of ensuring safety in the use of flammable gases.

The flammability limits of methane, propane, propylene, methyl formate, and 1,1-difluoroethane are adequately explained by the extended Le Chatelier's formula using a common set of parameter values. Table 2.6 shows the results obtained.